GENERATION AND REACTIONS OF DIPHENYLCARBENE ANION RADICAL ($Ph_2C^{\cdot-}$) IN THE GAS PHASE USING A FLOWING AFTERGLOW APPARATUS

by

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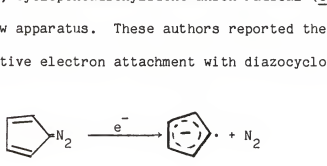
I. Introduction

The study of reactive intermediates is an important and fascinating area in organic chemistry. Carbene anion radicals (1) are an interesting group of coordinatively unsaturated intermediates. Formally, 1 has a pair of electrons and a spin unpaired electron on the central carbon atom. Thus, 1 should react as a base, a nucleophile, and/or a radical.

1

In 1966, Webster[1] described the formation of tetracyanocyclopentadienylidene anion radical ($(NC)_4C_5^{\cdot-}$) in the polarographic reduction of tetracyanodiazocyclopentadiene. McDonald, Hawley, and their coworkers[2] suggested that diphenylcarbene ($Ph_2C^{\cdot-}$) and fluorenylidene ($Fl^{\cdot-}$) anion radicals were the principle reactive intermediates in the electrochemical reduction of the corresponding diazoalkanes. These latter authors noted that carbene anion radicals were a subset of reactive intermediates termed "hypovalent ion radicals" (HIR) which were defined as a neutral or charged radical species containing less than the number of attached substituents found in the uncharged, free radical system normally associated with the central atom in the radical. However, recent studies by Parker and Bethell[3] have suggested that the proposed carbene anion radicals, $Ph_2C^{\cdot-}$ and $Fl^{\cdot-}$, were not important intermediates in the cathodic reduction of the respective diazoalkanes. Instead, the diazoalkane anion radicals ($R_2CN_2^{\cdot-}$) appeared to be the primary intermediates in the product forming channels. More recently, Bethell, et al.,[4] claimed the first formation of a carbene anion radical in solution by electrochemical reduction of azibenzil ($PhCOC(N_2)Ph$) in acetonitrile solution.

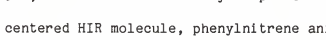
Obviously, studies of the chemistry of HIR species in the condensed phase are plagued by several major problems including (a) is the HIR species or a precursor anion radical the reactant, and (b) if the HIR molecule is formed, will the reaction with solvent overwhelm the desired reaction with added reactants. Both of these problems can be eliminated by generating the HIR species and determining its chemistry in the gas phase. In 1980, McDonald and coworkers[5] reported their first gas-phase studies of a HIR molecule, cyclopentadienylidene anion radical ($\underline{c}$-$C_5H_4^{\cdot -}$), using a flowing afterglow apparatus. These authors reported the generation of c-$C_5H_4^{\cdot -}$ by dissociative electron attachment with diazocyclopentadiene (eq 1), and



(1)

determination of its thermochemical properties (PA, H-atom affinity, and ΔH_f°) and ion-molecule reactions with a number of neutral molecules.

In 1981, McDonald and Chowdhury[6] reported their studies of a related nitrogen centered HIR molecule, phenylnitrene anion radical ($PhN^{\cdot -}$), generated in the gas phase by dissociative electron attachment with phenyl azide (eq 2). $PhN^{\cdot -}$ was especially interesting since it had a lower PA and

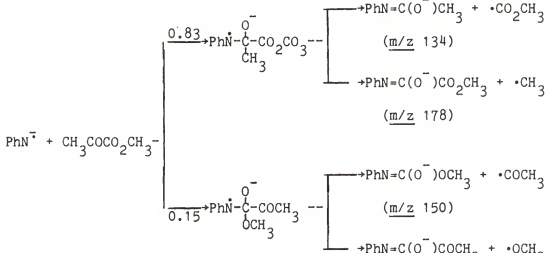


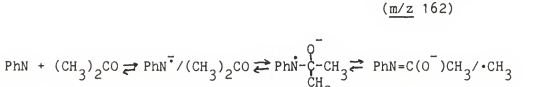
(2)

much lower H-atom affinity compared to $\underline{c}$-$C_5H_4^{\cdot -}$,. Thus, the reactions of $PhN^{\cdot -}$ with variety of organic carbonyl compounds could be studied. A major product forming channel in these reactions was nucleophilic addition of $PhN^{\cdot -}$ to carbonyl group and subsequent radical β-fragmentation of one attached

group from the tetrahedral adduct was observed. From the product mass spectrum, the relative and absolute reactivity of each individual channel was determined. For example, the reaction of $PhN^{\cdot-}$ with methyl pyruvate produced 86% keto-carbonyl addition/fragmentation and 12% ester-carbonyl addition/fragmentation along with 2% H^+-transfer product (eq 3).[6] The relative reactivity in the carbonyl compounds in the addition/fragmentation reactions was shown to be aldehydes > ketones > esters with similar substituent groups.

These authors also observed small signals for several total adduct species in the reactions of $PhN^{\cdot-}$ with some ketones. They suggested that these adducts were bound tetrahedral intermediates (3), not the loose complexes (2) or (4) shown in eq 4. The suggested mechanism involved a triple-minimum potential surface, shown in eq 4 with acetone as the carbonyl containing neutral reactant.





This was confirmed in their late study of the reaction of CF_3^- with $(CF_3)_2CO$ by determining that the PA of the adduct $(CF_3)_3CO^-$ was that of the authentic alkoxide.[7]

More recently, McDonald, et al.,[8] reported the gas-phase generation of 1,1,1,-3,3,3-hexafluoroisopropylidene anion radical $[(CF_3)_2C^{\cdot-}]$ from the diazo compound, $(CF_3)_2CN_2$, by dissociative electron attachment and the determination of its thermochemical properties.

Gas-phase studies of carbene and nitrene anion radicals have provided unambiguous information on the reactivities of these species. There are four major reasons why the study of gas-phase chemistry is important. First, in solution chemistry, solvents play significant, often dominant, roles in ionic reactions. In the gas phase, the intrinsic ion-molecule reaction process is determined without solvation and counterion complications. The differences in these results then are attributed to the effects of the condensed phase medium. For example, Bohme, et al.,[9] reported that the kinetic nucleophilicity of a series of oxy-anions RO^- is lowered significantly by solvation, $RO^-(HIR)_n$, in S_N2 displacement reactions with CH_3Br and CH_3Cl.

Second, gas-phase reactions can provide direct information about important reaction intermediates which are often suspected or assumed in the condensed phase. The studies of organic cations in the gas phase have a long history dating from the earliest days of mass spectropmetry.[10] More recently, instrumental development has made it possible to study organic anions in the gas phase.[11] The gas phase reactions of $PhN^{\cdot-}$ with carbonyl containing molecules[6] proceed by reaction channels which have no counterparts in the condensed phase. These results have significantly aided our understanding of gas phase nucleophilic addition reactions at the

carbonyl groups of organic substrates. The present work will continue these investigations of carbene anion radicals.

A third reason is that kinetic, thermochemical, and product data for gas-phase reactions are necessary for testing and refining reaction potential energy surfaces. The study of gas-phase S_N2 reactions was significant in Braumann's development of double-well potential surface with either symmetric or unsymmetric ion-dipole complexes as minima separated by the transition state barrier.[12] Kebarle and coworkers[13] carried out kinetic studies of S_N2 reactions at various temperatures and showed that these reactions could show either positive, negative, or no temperature effect depending upon the relative energy of the transition state. Carrion and Dewar[14] have carried out MNDO calculations for S_N2 reactions of chloride ion with alkyl chlorides using data obtained from gas-phase ion-molecule reaction studies. They found out that the central carbon is positively charged in the S_N2 transition state; thus, electron-donating groups should stabilize the transition state. The retardation on rate due to alkyl substitution on C_α was attributed to steric effects alone.

The fourth reason for these studies is that thermochemical properties for individual species of interest can be measured in the gas phase. The absolute acidities and basicities of many organic compounds, as well as their heat of formation have been measured in the gas phase.[15] These thermochemical data are essential for understanding how and why gas-phase reactions occur. One of the objectives of this work is to measure the proton affinity (PA) and heat of formation (ΔH_f°) of diphenylcarbene anion radical ($Ph_2C^{\cdot-}$).

One important factor that has aided for the dramatic growth in gas-phase ion chemistry has been in the area of instrumentation development.

Several different techniques have become available to the gas-phase chemists including (a) high pressure mass spectrometry (HPMS)[16], (b) ion cyclotron resonance spectrometry (ICR)[17], (c) ion beam technique[18], (d) the flowing afterglow apparatus (FA)[19]. Each of these techniques offers its own unique features. The first use of FA to obtain quantitative data on ion-neutral reactions was in 1963.[20] Several of the advantages and features of FA apparatus are listed below.

(i) Ions and neutral molecules have Maxwell-Boltzmann thermal energy distributions.

(ii) Multiple-step synthesis of ions is possible so that a great variety of ionic and neutral reactants can be studied.

(iii) Ion sources are readily varied from "cool" to "hot" (thermal electron attachment to microwave discharge and electron impact).

(iv) Accurate kinetic measurements can be readily made since reaction time is given by (length of the flow tube)/(average transport velocity of the buffer gas).

(v) Identification of neutral products is possible in some cases (emission spectroscopy or physical isolation).

(vi) Heating or cooling of the flow tube and of the buffer gas gives temperature dependence of reactions.

(vii) Collisional stabilization by buffer gas mimics inert solvent effects in the condensed phase reactions.

II. Objectives

The objectives of this investigation are (1) to generate diphenylcarbene anion radical ($Ph_2C^{\cdot-}$), a highly reactive hypovalent anion radical, in the gas phase, (2) to determine the proton affinity (PA) and heat of formation (ΔH_f°) of $Ph_2C^{\cdot-}$, (3) to study the reactivity of $Ph_2C^{\cdot-}$ with a variety of organic and inorganic molecules by determination of kinetics and product ion branching fractions, and (4) to compare the nucleophilicity of $Ph_2C^{\cdot-}$ towards sp^3 and sp^2 carbon with other hypovalent anion radicals and various closed shell anions.

The flowing afterglow apparatus is chosen to carry out the investigation. The generation of $Ph_2C^{\cdot-}$ will be accomplished by electron dissociative attachment with diazodiphenylmethane (Ph_2CN_2). The bracketing method will be used to determine the PA of $Ph_2C^{\cdot-}$. A variety of organic carbonyl compounds and methyl derivatives (CH_3X) will be allowed to react with $Ph_2C^{\cdot-}$, therefore, the gas-phase chemistry of $Ph_2C^{\cdot-}$ will be determined.

III. Experimental Method

The FA apparatus (Figure 1) used in this investigation has been described recently in the literature.[5] Gas-phase anions are prepared by dissociative electron attachment (DEA) in the upstream end of the stainless steel flow tube (120 x 7.15 cm i.d.) by adding small amounts of neutral reagent gases to the helium buffer gas and flowing this mixture past the electron gun. Alternatively, the anion of interest could be generated by an ion-molecule reaction between the ion produced by DEA with a second neutral reagent added through a port located just downstream of the electron gun. The flow pressure (P_{He}) and the flow velocity ($\underline{v}$) were maintained in the flow tube by a Stokes Roots blower-mechanical pump system (Model 1722-S) and can be varied from P_{He} = 0.2 to 1.2 torr and $\underline{v}$ 30 to 80 m s^{-1} by throttling a gate valve and/or altering the helium inlet flow. The first 25 cm of the flow tube downstream from the electron gun is a region for ion production and thermalization. The remaining 62.5 cm of the flow tube between the neutral inlet and the first sampling nose cone is the ion-molecule reaction region. The standard operating conditions are P_{He} = 0.5 torr and $\underline{v}$ = 80 m s^{-1} at 298°K. A quadrupole mass spectrometer operating at low pressure in a differentially pumped compartment monitors the ion composition of the flow.

In the present experiments, a large flow of helium buffer gas was purified by passage through two traps filled with Davison 4A molecular sieves cooled with liquid nitrogen. After warming to room temperature in a glass coil, the buffer gas entered the upstream end of the flow tube and was dispersed through a glass fritted disk funnel. A fast helium flow (80 m s^{-1}) was established in the flow tube by means of the Stokes Roots blower-mechanical pump system. The He flow was measured with a tri-flat flowmeter (Fisher & Porter, #449-306). The calibration data supplied by the

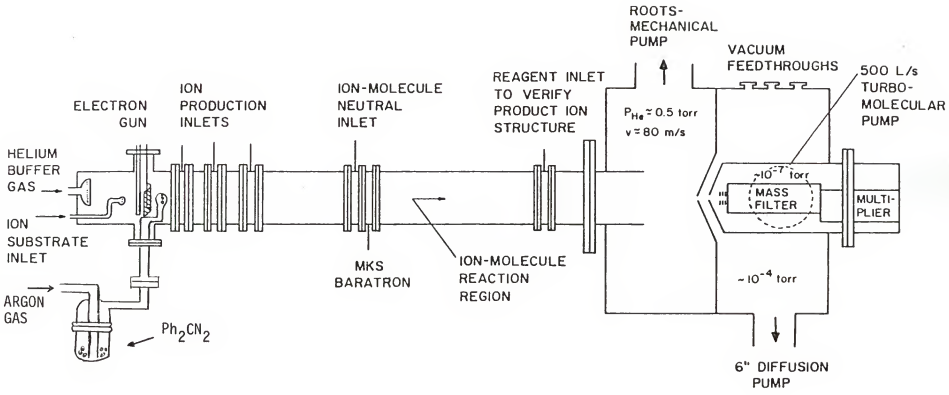


Figure 1. The Flowing Afterglow Apparatus.

manufacturer was used without further testing. With a helium flow of 200 atm cm^3 s^{-1} and partially throttled pumping speed, the helium pressure in the flow was typically 0.5 torr. $Ph_2C^{\cdot-}$ was generated from diphenyldiazomethane (Ph_2CN_2) by DEA in the upstream end of the flow tube. This was accomplished by adding small amounts of Ph_2CN_2 to the helium buffer gas and flowing the mixture past the electron gun. Most (~90%) of the electrons were attached by Ph_2CN_2 to form $Ph_2C^{\cdot-}$ (m/z 166) and N_2 (eq 5).

$$Ph_2CN_2 \xrightarrow{e^-} \underset{(m/z\ 166)}{Ph_2C^{\cdot-}} + N_2 \qquad (5)$$

However, a small fraction of electrons was detected (by adding SF_6 and observation of SF_6^-) in the downstream end of the flow tube. Sufficient Ph_2CN_2 could not be added to attach all electrons due to the secondary reaction between Ph_2CN_2 and $Ph_2C^{\cdot-}$ forming $Ph_2C{=}N{-}N{=}CPh_2^{\cdot-}$ (m/z 360) (eq 6).

$$Ph_2C^{\cdot-} + Ph_2CN_2 \xrightarrow{He} \underset{(m/z\ 360)}{Ph_2C{=}N{-}N{=}CPh_2^{\cdot-}} \qquad (6)$$

Since Ph_2CN_2 is a solid at room temperature (mp 30°C), the addition of Ph_2CN_2 was accomplished by sweeping a small stream of argon gas through a glass reservoir containing the solid Ph_2CN_2. The amount of Ph_2CN_2 added to the flow tube was controlled by adjusting the argon flow rate. A stream of N_2 (~10^{13} molecules cm^{-3}) was added through a port immediately downstream of the electron gun to remove the metastable helium atoms (He*). The presence of electrons downstream could mean that some $Ph_2C^{\cdot-}$ molecules were produced throughout the length of the flow tube. This could make the measured rate

constants lower limit of the true reaction rate constants. However, since less than 5% of the total number of electrons were involved and the accuracy of the rate constants are usually considered to be ± 30%, no additional corrections were applied. The flow concentration of the neutral reagent was measured by diverting the flow of the reagent from the flow tube to an evacuated flask and determining the increase of pressure in the calibrated volume as a function of time.

At P_{He} = 0.5 torr and $\underline{v}$ = 80 m s^{-1}, the concentration of helium is 1.6 x 10^{16} atoms cm^{-3}, that of the neutral reagent is ~10^{11} molecules cm^{-3}, and that of $Ph_2C^{\cdot-}$ is estimated to be <10^{8} molecules cm^{-3}, Pseudo-first-order kinetic conditions apply and the bimolecular rate constants are calculated using eq 7, where $[I^-]$ is the ion signal of $Ph_2C^{\cdot-}$ in arbitrary units, [N] is

$$k(cm^3\ molecule^{-1}\ s^{-1}) = \frac{d(\log)[I^-] \times F_{He}(atm\ cm^3\ s^{-1}) \times 2.78 \times 10^3}{d[N](molecules\ cm^{-3}) P_{He}(torr) \times \pi r^2 \times D(cm)} \quad (7)$$

the neutral reagent concentration, F_{He} and P_{He} are the flow and pressure of the helium buffer gas, respectively, r is the radius of the flow tube (7.15 cm), and D is the distance from the neutral reagent inlet to the first sampling nose cone (62.5 cm). The constant in eq 7 (2.303 x 760 torr atm^{-1} x 1.59) contains the parabolic flow correction of 1.59.[21]

Mass spectra of the negative ions present in the flow before and after the addition of neutral reagent were taken. Spectra are observed on an oscilloscope, and recorded and stored on disk using an Apple IIe computer. At least five separate spectra were taken and averaged to obtain the average spectrum for each point. Each averaged spectrum was baseline corrected on the computer prior to integration of starting and product ion signals to obtain the relative ion intensities as a function of the concentration of

the neutral reactant added. Usually six points were taken with changing concentration of added neutral reactant for each kinetic run. The rate constants measured in this work are averages from at least four separate kinetic runs taken on different days with different samples of neutral reagents loaded in the gas storage bulbs.

The helium gas used in this study was 99.99% purity and was supplied by Welders Products. All of the gas and liquid neutral reactants used were obtained from commercial sources (Fisher, Eastman, Aldrich, Matheson, and PCR). The liquid substrates were freshly distilled, and a constant boiling, center-cut fraction was used in the experiments. These liquid fractions were transferred to the gas storage bulbs after three freeze-pump-thaw degassing cycles. The gas substrates were used without further purification.

Diphenyldiazomethane was prepared according to the procedure described by Miller.[32] The diazo compound is stable at room temperature, mp 29-30°C, and its appearance is dark red crystals. The IR and ^{1}H NMR spectra correspond with those expected for this structure.

IV. Experimental Results

Pseudo-first-order decay of the log ion signal of $Ph_2C^{\cdot-}$ (m/z 166) vs. concentration of neutral reactants were observed in all reactions. A typical semilog plot is shown in Figure 2 for the reaction of $Ph_2C^{\cdot-}$ with $CF_3CO_2CH_3$ (eq 8). Figure 2 shows the typical range of neutral reactant

$$Ph_2C^{\cdot-} + CF_3CO_2CH_3 \xrightarrow{0.85} Ph_2C{=}C(O^-)CF_3 + CH_3O\cdot \quad (m/z\ 263) \qquad (8a)$$

$$\xrightarrow{0.13} Ph_2C{=}C(O^-)OCH_3 + F_3C\cdot \quad (m/z\ 225) \qquad (8b)$$

$$\xrightarrow{0.02} CF_3CO_2^- + PH_3\dot{C}CH_3 \quad (m/z\ 113) \qquad (8c)$$

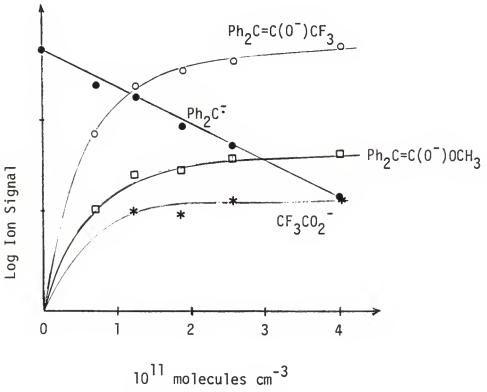


Figure 2. Semilogarithmic plot of decay of $Ph_2C^{\cdot-}$ and formation of product ions for the reaction of $Ph_2C^{\cdot-}$ with $CF_3CO_2CH_3$.

concentrations that were used for such fast reactions. Each point in the plot is the integrated peak area of the ion signals observed from the mass spectrum in arbitrary units.

The kinetic and product data for the ion-molecule reactions of $Ph_2C^{\cdot-}$ are summarized in Table I. The measured rate constants (k_{total}'s) are estimated to be accurate to ± 30%.[5] Errors quoted for the rate constants are standard deviations from the average of multiple runs and are generally 10% of k_{total} unless specifically noted. The collision rate constants (k_{ADO}'s) were calculated using the average dipole orientation theory[23] (eq i), where q is the charge of the ion, μ is the reduced mass of the ion and

$$k_{ACO} = \frac{2\pi q}{\mu^{1/2}} [\alpha^{1/2} + c\mu_D(\frac{2}{\pi kT})^{1/2}] \qquad (i)$$

the neutral molecule ($\mu = m_1m_2/(m_1 + m_2)$), α is the polarizablility of the neutral molecule, c is a constant determined by the average dipole orientationn of the neutral molecule, μ_D is the dipole moment of the neutral molecule, k is the Boltzmann constant, and T is the absolute temperature. If the dipole moment of the neutral reactant is unknown, the Langevin collision rate constants were calculated instead[23] (eq ii). The reaction efficiencies are the fractions of collisions which result in reaction

$$k_{Langevin} = 2\pi q(\alpha/\mu)^{1/2} \qquad (ii)$$

(reaction efficiency = k_{total}/k_{ACO}). The reaction enthalpies were calculated from thermochemical data from references 15, 24, 25, 26, 27, and this work.

Table I. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of Diphenylcarbene Anion Radical ($Ph_2C^{\cdot-}$)

Rxn	Neutral Reactants	Product Ion + [Assumed Neutral]	Fraction of Product Ion Signal	$-\Delta H°$,[a] kcal mol^{-1}	k_{total},[b] cm^3 $molecule^{-1}$ s^{-1}	k_{ADO},[c] cm^3 $molecule^{-1}$ s^{-1}	Reaction Efficiency[d]
1	$HC{\equiv}CH$	$HC{\equiv}C^-$ + $[Ph_2CH\cdot]$	1.00	4.6	3.7×10^{-10}	8.7×10^{-10}	0.43
2	$C_3H_7C{\equiv}CH$	$C_3H_7C{\equiv}C^-$ + $[Ph_2CH\cdot]$	1.00	1.7	1.6×10^{-10}	1.0×10^{-9} [e]	0.16
3	$CH_3C{\equiv}CH$	$CH_3C{\equiv}C^-$ + $[Ph_2CH\cdot]$	1.00	0.4	1.9×10^{-11} [f]	1.2×10^{-9}	0.017
4	$(CH_3)_2CHOH$	$(CH_3)_2CHO^-$ + $[Ph_2CH\cdot]$	1.00	5.9	6.3×10^{-10}	1.3×10^{-9}	0.48
5	C_2H_5OH	$C_2H_5O^-$ + $[Ph_2CH\cdot]$	1.00 [g]	3.9	8.5×10^{-10}	1.4×10^{-9}	0.61
6	CH_3OH	CH_3O^- + $[Ph_2CH\cdot]$	1.00 [g]	0.8	1.0×10^{-9}	1.4×10^{-9}	0.71
7	$C_6H_5CH(CH_3)_2$	$C_6H_5C^-(CH_3)_2$ + $[Ph_2CH\cdot]$	1.00	2.5	not measured		
8	$C_6H_5CH_3$	$C_6H_5CH_2^-$ + $[Ph_2CH\cdot]$	1.00	1.0	not measured		
9	$p\text{-}CH_3C_6H_5CH_3$	no reaction		-0.5[h]			
10	$CH_3CH{=}CH_2$	no reaction		-10.0[h]			
11a	CH_3CHO	$Ph_2C{=}C(O^-)H$ + $[CH_3\cdot]$	0.50	22.0	8.8×10^{-10}	1.8×10^{-9}	0.49
11b		$CH_2{=}C(O^-)H$ + $[Ph_2CH\cdot]$	0.50	13.6			
12a	C_2H_5CHO	$Ph_2C{=}C(O^-)H$ + $[C_2H_5\cdot]$	0.54	24.5	8.2×10^{-10}	1.7×10^{-9}	0.48
12b		$CH_3CH{=}C(O^-)H$ + $[Ph_2CH\cdot]$	0.46	14.1			
13	$(CH_3)_3CCHO$	$Ph_2C{=}C(O^-)H$ + $[(CH_3)_3C\cdot]$	1.00	28.0	6.5×10^{-10}	9.8×10^{-10} [e]	0.66
14a	CH_3COCH_3	$CH_3C(O^-){=}CH_2$ + $[Ph_2CH\cdot]$	0.90	11.2	6.3×10^{-10}	1.8×10^{-9}	0.35
14b		$Ph_2C{=}C(O^-)CH_3$ + $[CH_3\cdot]$	0.10	20.5			
15	CF_3COCH_3	$CF_3C(O^-){=}CH_2$ + $[Ph_2CH\cdot]$	1.00	29.7	1.0×10^{-9}	9.1×10^{-10} [e]	1.00

Table I. (Continued)

16a	$CH_3COCOCH_3$	$CH_3COC(O^-)=CH_2$ + $[Ph_2CH\cdot]$	0.77	18.0	9.4×10^{-10}	8.8×10^{-10}	1.00
16b		$Ph_2C=C(O^-)CH_3$ + $[CH_3CO\cdot]$	0.23	32.5			
17a	$CH_3CO_2CH_3$	$CH_2=C(O^-)OCH_3$ + $[Ph_2CH\cdot]$	0.97	9.0	1.3×10^{-10}	1.3×10^{-9}	0.10
17b		$Ph_2C=C(O^-)CH_3$ + $[CH_3O\cdot]$	0.03	7.0			
18	HCO_2CH_3	$Ph_2C=C(O^-)H$ + $[CH_3O\cdot]$	1.00	12.0	1.6×10^{-10}	1.4×10^{-9}	0.11
19a	$CF_3CO_2CH_3$	$Ph_2C=C(O^-)CF_3$ + $[CH_3O\cdot]$	0.81	25.0	1.0×10^{-9}	1.4×10^{-9}	0.71
19b		$Ph_2C=C(O^-)OCH_3$ + $[CF_3\cdot]$	0.14	23.0			
19c		$CF_3CO_2^-$ + $[Ph_2\dot{C}CH_3]$	0.05	72.5			
20a	$CF_3CO_2C_2H_5$	$Ph_2C=C(O^-)CF_3$ + $[C_2H_5O\cdot]$	0.90	22.5	7.0×10^{-10}	1.2×10^{-9}	0.58
20b		$Ph_2C=C(O^-)OC_2H_5$ + $[CF_3\cdot]$	0.10	20.0			
21a	$CF_3COSC_2H_5$	$Ph_2C=C(O^-)CF_3$ + $[C_2H_5S\cdot]$	0.45	44.0	8.8×10^{-10}	1.3×10^{-9}	0.66
21b		CF_3COS^- + $[Ph_2CC_2H_5]$	0.45	78.0			
		or $[Ph_2CH\cdot + CH_2=CH_2]$		48.0			
21c		$CF_3COSCH^-CH_3$ + $[Ph_2CH\cdot]$	0.10				
22a	$CH_3COCO_2CH_3$	$CH_3OCOC(O^-)=CH_2$ + $[Ph_2CH\cdot]$	0.33	15.0	1.0×10^{-9}	8.9×10^{-10} e	1.00
22b		$Ph_2C=C(O^-)CH_3$ + $[CH_3OCO\cdot]$	0.54	25.0			
22c		$Ph_2C=C(O^-)COCH_3$ + $[CH_3O\cdot]$	0.08	17.0			
22d		$Ph_2C=C(O^-)OCH_3$ + $[CH_3CO\cdot]$	0.05	34.0			
23	CH_3Br	Br^- + $[Ph_2\dot{C}CH_3]$	1.00	65.5	3.9×10^{-10}	1.1×10^{-9}	0.35
24	CH_3Cl	Cl^- + $[Ph_2\dot{C}CH_3]$	1.00	60.0	3.2×10^{-11}	1.3×10^{-9}	0.025

Table I. (Continued)

25	C_2H_5Br	$Br^- + [Ph_2\dot{C}C_2H_5]$	1.00	66.4	1.3×10^{-10}	1.2×10^{-9}	0.11
		or $[Ph_2CH\cdot + CH_2{=}CH_2]$		40.0			
26	C_2H_5Cl	$Cl^- + [Ph_2\dot{C}C_2H_5]$	1.00	61.0	1.4×10^{-12}	1.5×10^{-9}	0.0009
		or $[Ph_2CH\cdot + CH_2{=}CH_2]$		32.0			
27a	CO_2 (+ He)	$Ph_2CCO_2^-$	0.99		3.9×10^{-10}	6.5×10^{-10}	0.60
27b		$Ph_2CO^- + [CO]$	0.01				
28a	COS (+ He)	Ph_2CCOS^-	0.85		4.4×10^{-10}	9.4×10^{-10}	0.47
28b		$Ph_2CS^- + [CO]$	0.15				
29a	CS_2 (+ He)	$Ph_2CCS_2^-$	0.04		7.1×10^{-10}	9.6×10^{-10}	0.74
29b		$Ph_2CS^- + [CS]$	0.96				
30a	O_2 (+ He)	$Ph_2CO_2^-$	0.29 [i]		4.8×10^{-11}	5.7×10^{-10}	0.08
30b		$PhCO_2^- + [Ph\cdot]$	0.36	112.0			
30c		$PhO^- + [PhCO\cdot]$	0.21	96.0			
30d		$Ph^- + [Ph\cdot + CO_2]$	0.10	49.0			
30e		$O^- + [Ph_2C{=}O]$	0.04				

[a] Enthalpies of reaction were calculated from thermochemical data from the following sources. Heats of formation of CF_3COCH_3, $HC{\equiv}CH$, $C_3H_7C{\equiv}CH$, $CH_3C{\equiv}CH$, $(CH_3)_2CHOH$, C_2H_5OH, CH_3OH, $C_6H_5CH(CH_3)_2$, $C_6H_5CH_3$, $p\text{-}CH_3C_6H_4CH_3$, $CH_3CH{=}CH_2$, CH_3CHO, C_2H_5CHO, CH_3COCH_3, $CH_3CO_2CH_3$, and Ph_2CH_2 and their corresponding conjugate bases are from ref. 15 and of $CH_3COCOCH_3$ is from ref. 24. Heats of formation of HCO_2CH_3, alkyl halides, and the inorganic compounds are from ref. 25. Heats of formation of $(CH_3)_3CCHO$, $CF_3CO_2CH_3$, $CF_3CO_2C_2H_5$, $CF_3COSC_2H_5$, and $CH_3COCO_2CH_3$ were calculated by group

Table I. (Footnotes continued)

additivity (ref. 25). Heats formation of radicals are from ref. 26 except that of $CH_3O\cdot$ (EA = 39.4 ± 1.4 kcal mol^{-1}) is from ref. 27. $\Delta H_f^\circ(Ph_2C^{\cdot-})$ = 84 ± 2 kcal mol^{-1}(this work). $\Delta H_f^\circ(Ph_2C{=}C(O^-)H)$ = -12 ± 4 kcal mol^{-1} (calculated based on $\Delta H_f^\circ(Ph_2CHCHO)$ = 13.2 kcal mol^{-1} (group additivity) and and estimated ΔH°_{acid} (Ph_2CHCHO) = 342 kcal mol^{-1}. $\Delta H_f^\circ(Ph_2C{=}C(O^-)CH_3$ = -22.0 kcal mol^{-1} (calculated based on $\Delta H_f^\circ(Ph_2CHCOCH_3)$ = 0.84 kcal mol^{-1} (group additivity) and estimated $\Delta H^\circ_{acid}(Ph_2CHCOCH_3)$ = 344 ± 4 kcal mol^{-1}). $\Delta H_f^\circ(Ph_2C{=}C(O^-)OCH_3)$ = -67 ± 4 kcal mol^{-1} (calculated based on $\Delta H_f^\circ(Ph_2CHCO_2CH_3)$ = -46 kcal mol^{-1} (group additivity) and estimated $\Delta H^\circ_{acid}(Ph_2CHCO_2CH_3)$ = 346 kcal mol^{-1}). $\Delta H_f^\circ(Ph_2C{=}C(O^-)CF_3)$ = -182 ± 4 kcal mol^{-1} (calculated based on $\Delta H_f^\circ(Ph_2CHCOCF_3)$ = -141.5 kcal mol^{-1} (group additivity) and estimated $\Delta H^\circ_{acid}(Ph_2CHCOCF_3)$ = 326 kcal mol^{-1}). $\Delta H_f^\circ(Ph_2\dot{C}C_2H_5)$ = 52 ± 4 kcal mol^{-1}(estimated based on $\Delta H_f^\circ(Ph_2\dot{C}CH_3)$ = 60.9 kcal mol^{-1} (ref. 26b), $\Delta H_f^\circ(CH_3\cdot)$ = 34 kcal mol^{-1}, and $\Delta H_f^\circ(C_2H_5\cdot)$ = 26 kcal mol^{-1}). [b] k_{total}'s are estimated to be accurate to ±30%. Errors of maximum deviation from the average of multiple runs are within ± 0.5 unless specifically noted. [c] The collision rate constants (k_{ADO}'s) were calculated by using the average dipole orientation theory (ref. 23). [d] The reaction efficiency is the fraction of collisions which result in reaction (k_{total}/k_{ADO}). [e] Calculated Langevin collision rate constants (ref. 23) since the dipole moment of the neutral is unknown. [f] It was found that the $CH_3C{\equiv}CH$ used in this experiment contained some 14 ± 5% of $HC{\equiv}CH$. The rate constant reported is a rough approximation based on the experimental rate constant ($k = 7.3 \times 10^{-11}$ $cm^3 molecule^{-1}$ s^{-1}). See text for details. [g] The percent recovery of product ions from reaction 5 was 65% and from reaction 6 was only 5%. See text for details. [h] Calculated assuming H^+-transfer occured. [i] Helium buffer gas effect was observed, i.e. apparent rate constant changes with pressure.

V. Discussion

A. Proton Transfer Reactions of $Ph_2C^{\cdot-}$ with HA Molecules.

Determination of PA and ΔH_f° of $Ph_2C^{\cdot-}$. It is imperative to determine the ΔH_f° of any new intermediate species in order to predict and understand its chemistry. For anionic species, this is generally accomplished by experimentally determining the proton affinity (PA) of the anion from which the ΔH_f° can be calculated. The PA of the anion is bracketed as tightly as possible by adding a series potential H^+-donor neutral molecules of known gas-phase acidity[15] to the flow reactor and measuring the rate constants. The PA of the anion is bracketed between the ΔH°_{acid}'s of the pair of potential H^+-donors where H^+-transfer is observed with one but not the other of the pair. Proton transfer was judged to have occurred by a decrease in the intensity of $Ph_2C^{\cdot-}$ (m/z 166) ion signal and formation of the corresponding ion signal for the conjugate base A^- (eq 9). The data for

$$Ph_2C^{\cdot-} + HA \longrightarrow A^- + Ph_2CH\cdot \qquad (9)$$

bracketing PA($Ph_2C^{\cdot-}$) is listed in Table II.

Table II. Data for Bracketing PA(Ph_2C^-) in H^+-Transfer Reactions with HA Molecules of Known Acidity.[15]

Rxn[a]	HA	Product Ion[a]	H^+-Transfer?	ΔH°_{acid}(HA), (kcal mol^{-1})
1	HC≡CH	$HC{\equiv}C^-$	Yes	377.6 ± 2
2	$n\text{-}C_3H_7C{\equiv}CH$	$n\text{-}C_3H_7C{\equiv}C^-$	Yes	380 ± 2
7	$C_6H_5CH(CH_3)_2$	$C_6H_5C(CH_3)_2^-$	Yes	379.7 ± 2
9	$C_6H_5CH_3$	$C_6H_5CH_2^-$	Yes	381.2 ± 2
3	$CH_3C{\equiv}CH$	$CH_3C{\equiv}C^-$	Yes	381.3 ± 2
6	CH_3OH	CH_3O^-	Yes	381.4 ± 0.6
9	$\underline{p}\text{-}CH_3C_6H_4CH_3$		No	382.7 ± 2
10	$CH_3CH{=}CH_2$		No	390.8 ± 2
11	H_2O		No	390.8 ± 2

[a]Data shown in Table I.

The fast H^+-transfer reaction of Ph_2C^- with HC≡CH (ΔH°_{acid} = 377.6 kcal mol^{-1}) produced exclusively the corresponding anion m/z 25 ($HC{\equiv}C^-$). When $CH_3C{\equiv}CH$ (ΔH°_{acid} = 381.8 kcal mol^{-1}) was allowed to react with Ph_2C^-, the rate constant ($k = 7.3 \times 10^{-11}$ cm^3 s^{-1}) (Fig. 3) for decay of Ph_2C^- was smaller than that for HC≡CH ($k = 3.7 \times 10^{-10}$ cm^3 s^{-1}) and two product ions, m/z 25 ($HC{\equiv}C^-$; 78%) and 39 ($CH_3C{\equiv}C^-$; 22%), were observed. Although a S_N2 displacement reaction of Ph_2C^- at methyl of $CH_3C{\equiv}CH$ is modestly exothermic (ΔH° = −5.0 ± 2 kcal mol^{-1}), it appeared that this mechanism would be an unlikely source of m/z 25 in this reaction. The electron impact (IE) mass sepctra[43] of HC≡CH and $CH_3C{\equiv}CH$ are quite different; EI with HC≡CH yield m/z 26 (r.a. 100) and 25 (r.a. 19) while EI with $CH_3C{\equiv}CH$ gave m/z 40 (r.a. 100), 26 (r.a. 3.4), and 25 (r.a. 4.3) as important ion signals. An EI mass

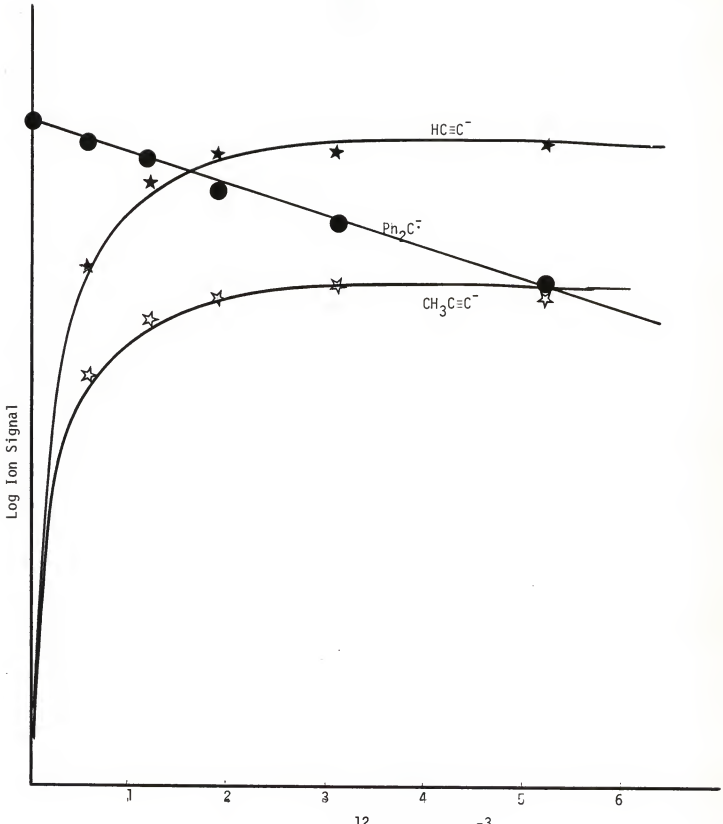


Figure 3. The decay of Ph_2C^- and the formation of $HC{\equiv}C^-$ and $CH_3C{\equiv}C^-$.
$k_{total} = 7.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

spectrum of the $CH_3C{\equiv}CH$ used in the above reaction with PH_2C^- was obtained and showed the presence of 14 ± 4% $HC{\equiv}CH$, assuming the same ionization efficiencies for $CH_3C{\equiv}CH$ and $CH{\equiv}CH$.

The observation of $CH_3C{\equiv}C^-$ as a product ion from the reaction of PH_2C^- with the mixture of $CH_3C{\equiv}CH$ (86%) and $HC{\equiv}CH$ (14%) requires $PA(Ph_2C^-) > PA(CH_3C{\equiv}C^-)$. The above data cannot be analyzed further to obtain the rate constant for H^+-transfer between Ph_2C^- with CH_3C CH since the rate constant for the exothermic secondary ion-molecule reaction (H^+transfer between $CH_3C{\equiv}CH$ and $HC{\equiv}CH$) is unknown. However, this rate is probably slow since a carbon-centered acid and base are involved.[44] The rate constant for the $CH_3C{\equiv}CH$ reaction can be estimated to be 10 to 20 times less than that of the $HC{\equiv}CH$ reaction. This reduction of the rate constant for H^+-transfer from reactions of Ph_2C^- with $HC{\equiv}CH$ and $CH_3C{\equiv}CH$ is expected as the $\Delta H°$ approaches zero.

The reaction between toluene and PH_2C^- was very slow ($<10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}). In order to observe the product ion (m/z 91, $C_6H_5CH_2^-$), the flow conditions of $\underline{v}$ = 40 m s^{-1} and P_{He} = 1.0 torr were required to increase the reaction time. The m/z 91 signal was weak, however, despite the fact that the toluene was added directly from a reservoir of the liquid. When CH_3O^- was allowed to react with toluene under these conditions, the m/z 91 signal was fairly intense [$PA(CH_3O^-)$ = 381.4 kcal mol^{-1}, $\Delta H°_{acid}(C_6H_5CH_3)$ = 381.3 kcal mol^{-1})[15]. These are only qualitative comparisons of a carbon-centered base vs. that of a oxygen-centered base. The reaction of Ph_2C^- with CH_3OH leads to a fast decay of Ph_2C^- signal, but only a weak signal of CH_3O^- was seen; for discussion of this reaction, see the next section. Nevertheless, Ph_2C^- did deprotonate $CH_3C{\equiv}CH$ ($\Delta H°_{acid}$ = 381.8 kcal mol^{-1})[15]

forming the corresponding anion $CH_3C{\equiv}C^-$, although the rate was slow. No reaction was observed between Ph_2C^- with $\underline{p}CH_3C_6H_4CH_3$, $CH_3CH{=}CH_2$, or H_2O. From these experimental results, $PA(Ph_2C^-) = 382 \pm 2$ kcal mol^{-1} is assigned. Using $\Delta H_f^\circ(Ph_2CH\cdot) = 69 \pm 2$ kcal mol^{-1},[26b] $\Delta_f^\circ(Ph_2C^-) = 84 \pm 2$ kcal mol^{-1} was calculated by eq 10. Compared to Ph_2CH^- ($\Delta H^\circ_{acid} = 366.5$ kcal mol^{-1})[15], Ph_2C^-

$$\Delta H_f^\circ Ph_2C^-) = \Delta H_f^\circ(Ph_2CH\cdot) - \Delta H_f^\circ(H^+) + PA(Ph_2C^-) \qquad (10)$$

is a stronger base by ~15 kcal mol^{-1}.

B. Reactions of Ph_2C^- with Alcohols. Only H^+-transfer reactions were observed when Ph_2C^- was allowed to react with C_2H_5OH and $(CH_3)_2CHOH$ (eqs 11 and 12). These H^+-transfer reactions were fast and alkoxide-alcohol cluster ions were formed by secondary ion-molecule reactions. While the percent

$$Ph_2C^-\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2CHO^- + (CH_3)_2CHO^-/((CH_3)_2CHOH)_n + Ph_2CH\cdot \qquad (11)$$

$$Ph_2C^-\cdot + C_2H_5OH \longrightarrow C_2H_5O^- + C_2H_5O^-/(C_2H_5OH)_n + Ph_2CH\cdot \qquad n = 1,2 \qquad (12)$$

recovery of the product ions from reaction 11 were 90%, but that for eq 12 was only 65%, % recovery = (total ion signal intensity after adding ROH)/(ion signal intensity of Ph_2C^- before adding ROH). This indicated that some product forming channel was not detected in eq 12. When CH_3OH was allowed to react with Ph_2C^-, a fast decay of the Ph_2C^- signal was observed ($k_{total} = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}), along with formation of a small

signal at m/z 31; the percent recovery of m/z was about 5%. When SF_6 was added to the flow tube through an inlet located downstream from the CH_3OH inlet, formation of SF_6^- (m/z 146) was observed. If one stops adding CH_3OH, the SF_6^- signal immediately disappeared and the $Ph_2C^{-}\cdot$ signal reappeared. These observations indicate that CH_3OH reacts primarily with $Ph_2C^{-}\cdot$ forming some anion or anion radical which ejects an electron. The ejected electron then was attached by SF_6 added through the downstream inlet and SF_6^- was observed.

Considering the structures of the starting anion radical ($Ph_2C^{-}\cdot$) and the alcohol (CH_3OH), the ketyl anion radical of formaldehyde, $H_2CO^{-}\cdot$, appears to be the most likely candidate for the unobserved product anion or anion radical formed in this reaction. While the EA($CH_3O\cdot$) = 36.2 ± 0.5 kcal mol^{-1},[27] EA(H_2CO) = -19.8 kcal mol^{-1}, the latter being a sizeable negative value.[28] Thus, $H_2CO^{-}\cdot$ will be unstable with respect to autodetachment of an electron. This overall reaction of β-H_2^+ transfer from CH_3OH to $Ph_2C^{-}\cdot$ is believed related to the minor reaction channels of two other carbene anion radicals shown in eqs 13 and 14 where the product anion radicals, $H_2CS^{-}\cdot$ and $(CF_3)_2CO^{-}\cdot$, were directly observed (EA(neutral) is positive).[29]

$$(CF_3)_2C^{-}\cdot + CH_3SH \longrightarrow H_2CS^{-}\cdot + (CF_3)_2CH_2 \qquad (13)$$

$$CF_3CH^{-}\cdot + (CF_3)_2CHOH \longrightarrow (CF_3)_2CO^{-}\cdot + CF_3CH_3 \qquad (14)$$

To rationalize the present result with CH_3OH and $Ph_2C^{-}\cdot$, we first note that this process of β-H_2^+ transfer (H^+ and $H\cdot$) occurred at the collision limit (k_{total} is 70% of k_{ADO} in Table I, reaction 6). Simple H^+-transfer in the collision complex ($Ph_2C^{-}\cdot/HOCH_3$) is only 0.8 kcal mol^{-1} exothermic and would generally not be expected to yield such a fast rate of reaction.

However, the slightly exothermic H^+-transfer would appear to be a logical first step (assuming step-wise H_2^+-transfer) since H-atom transfer between $Ph_2C^-\cdot$ and CH_3OH ($DH°(Ph_2C^--H) = 96.4$ kcal mol^{-1}, $DH°(HOCH_2-H) = 95.9$ kcal mol^{-1},[26a] and $DH°(CH_3O-H) = 104 \pm 1$[26a]) approaches thermal neutrality and $Ph_2C^-\cdot$ did not show radical behavior with any other neutral reagent. However, the second step must be H-atom transfer according to eq 15. The problem here is that the overall process in eq 15 is only slightly

$$Ph_2C^-\cdot + HOCH_3 \rightleftharpoons Ph_2C^-\cdot/HOCH_3 \rightleftharpoons Ph_2CH\cdot/^-OCH_3 \rightarrow Ph_2CH_2 + H_2CO^-\cdot \qquad (15)$$

exothermic, $\Delta H°(15) = -2.3 \pm 2$ kcal mol^{-1},[15,24,27] which would not be expected to lead to a fast rate for this reaction. It is the autodetachment of the electron from $H_2CO^-\cdot$ giving H_2CO which leads to the overall process in eq 16 being considerably exothermic, $\Delta H°(16) = -22.3 \pm 2$ kcal mol^{-1}, the difference being the negative $EA(H_2CO)$. This leads to the stepwise formulation of the reaction in eq 17. The separation of the complex

$$Ph_2C^-\cdot + HOCH_3 \rightarrow Ph_2CH_2 + H_2CO + e^- \qquad (16)$$

$$Ph_2C^-\cdot + CH_3OH \rightleftharpoons Ph_2C^-\cdot/HOCH_3 \rightleftharpoons Ph_2C^-\cdot/^-OCH_3 \xrightarrow{0.05} Ph_2CH\cdot + CH_3O^- \qquad (17a)$$

$$\downarrow\uparrow$$

$$Ph_2CH_2/^-\cdot OCH_2 \xrightarrow{0.95} Ph_2CH_2 + H_2CO + e^- \qquad (17b)$$

($Ph_2CH\cdot/^-OCH_3$) to CH_3O^- and $Ph_3CH\cdot$ (17a) is expected to be slow, and in fact, only 5% CH_3O^- was observed. However, the channel of H-atom transfer followed by detachment of electron is much more exothermic and leads to the products of eq 17b.

This H_2^+-transfer process also explains the low percent recovery of $C_2H_5O^-$ ions observed in the reaction of $Ph_2C^{-\cdot}$ with C_2H_5OH (eq 12). Although the β-CH bonds in C_2H_5OH and in $C_2H_5O^-$ have lower DH°'s than that in CH_3OH, the additional exothermicity in H^+-transfer forming the complex $(Ph_2C\cdot/^-OC_2H_5)$ appears to effect more rapid separation of the products. This exothermicity of H^+-transfer would be even more effective with $(CH_3)_2CHOH$ as the H^+-donor, and an increased steric effect in the H-atom transfer process in this reaction results in exclusively H^+-transfer. While the exothermicities of the reaction of $Ph_2C^{-\cdot}$ with these three alcohols increase for both H^+-transfer (CH_3OH, $\Delta H° = -0.8$ kcal mol^{-1}; C_2H_5OH, $\Delta H° = -3.9$ kcal mol^{-1}; $(CH_3)_2CHOH$, $\Delta H° = -5.9$ kcal mol^{-1}) and H_2^+-transfer (CH_3OH, $\Delta H° = -22.3$ kcal mol^{-1}; C_2H_5OH, $\Delta H° = -27.8$ kcal mol^{-1}; $(CH_3)_2CHOH$, $\Delta H° = -30.8$ kcal mol^{-1}), the EA's of the corresponding carbonyl product of H_2^+-transfer decrease ($EA(H_2CO) = -19.8$ kcal mol^{-1}; $EA(CH_3CHO) = -27.4$ kcal mol^{-1}; $EA((CH_3)_2CO) = -34.8$ kcal mol^{-1})[28]. This latter point suggests that H_2^+-transfer becomes progressively more difficult if the ketyl anion radical is directly formed.

C. Reactions of $Ph_2C^{-\cdot}$ with Alkyl Halides and Other CH_3X Molecules. The bimolecular substitution reactions of anions with CH_3X molecules, termed the S_N2 reaction, has been studied widely in the condensed phase[30] and gas phase[31-34]. The same mechanism is considered to apply in both phases involving attack of the anion as a nucleophile at the backside of the carbon producing the neutral substitution product and the anionic leaving group, X^-. Inversion of configuration in the substitution product in the gas phase was established by Brauman, et al.[31] Bohme, et al.,[32] set up a scale of kinetic nucleophilicity based on rate constants and exothermicities for the reactions of a series anions with CH_3Br, CH_3Cl, and CH_3F. Pellerite and

Brauman,[33] have recently used Marcus theory and RRKM calculations to model gas-phase S_N2 reactions to estimate the intrinsic barriers for specific processes using the double minimum potential energy vs. reaction coordinate diagram shown in Figure 4.

In the present work, although the reaction of $Ph_2C^{-}\cdot$ with CH_3Br (reaction 23, Table I) yielding Br^- was fast ($k = 3.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), the related reaction of $Ph_2C^{-}\cdot$ with CH_3Cl (reaction 24, Table I) producing Cl^- occurred with only a modest rate constant ($k = 3.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). Based on Bohme's kinetic nucleophilicity scale[32], $Ph_2C^{-}\cdot$

$$X^- \; CH_3Y \rightleftharpoons X^-/CH_3Y \rightleftharpoons Y^-/CH_3X \rightleftharpoons Y^- + CH_3X$$

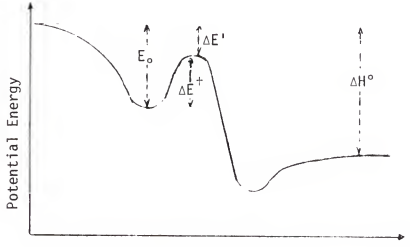


Figure 4. Potential energy vs. reaction coordinate diagram for an exothermic S_N2 reaction of X^- with CH_3Y. The well-depth for Cl^-/CH_3Cl is estimated to be 10 kcal mol^{-1} and depends on the polarizability and dipole moment of the neutral component.

must be considered to be at the lower end of those anions exhitibing medium nucleophilicity. The rather slow reaction of $Ph_2C^{-}\cdot$ with CH_3Cl requires that the barrier separating the collision complexes is substantial in spite of the large exothermicity for this reaction ($\Delta H^\circ = -60 \pm 2$ kcal mol^{-1}). This latter point is seen in that Ph_2C^{-} has a large methyl cation affinity ($Ph_2C^{-}\cdot + CH_3^+ \rightarrow Ph_2CCH_3$; $-\Delta H^\circ = 285$ kcal mol^{-1} = MCA($Ph_2C^{-}\cdot$))[34]. Using the Marcus formalism of Pellerite and Brauman[33], these data suggest that the S_N2 reaction of $Ph_2C^{-}\cdot$ with CH_3X molecules have large intrinsic barriers which are partially compensated for by the singificant exothermicities (MCA) of the reactions leading to the modest kinetic nucleophilicity of $Ph_2C^{-}\cdot$ observed.

Using the above conclusion, the reactions of $Ph_2C^{-}\cdot$ with various methyl esters should be interesting since carbonyl addition followed by radical β-fragmentation should easily compete with the slow alternate S_N2 reaction channel. This is exactly what is observed. The reaction of $Ph_2C^{-}\cdot$ with $CF_3CO_2CH_3$ (reaction 19, Table I) occurred at nearly the collision limit with only a small contribution from the highly exothermic S_N2 displacement product channel. The fast reaction of $Ph_2C^{-}\cdot$ with HCO_2CH_3 (reaction 18, Table I) and $CH_3CO_2CH_3$ (reaction 17, Table I) occurred exclusively by reaction channels other than S_N2 displacement. These results were qualitatively expected since $CF_3CO_2^{-}$ is a much better leaving group than either HCO_2^{-} or $CH_3CO_2^{-}$. The details of these reactions are discussed later.

In the condensed phase, methyl derivatives (CH_3X) react on the average 30 times faster than ethyl derivatives (C_2H_5X) in S_N2 displacement reaction.[35] The reaction of $Ph_2C^{-}\cdot$ with C_2H_5Br yielding Br^{-} (reaction 25, Table I) gave a rate constant three times smaller than that of the reaction

of $Ph_2C^{-}\cdot$ with CH_3Br. Both of these reactions occurred close to the collision limit (~ 10% of k_{ADO}), however. A better comparison of these alkyl effect is seen in the slower reactions of $Ph_2C^{-}\cdot$ with CH_3Cl and C_2H_5Cl. Here, the ratio of $k_{CH_3Cl}/k_{C_2H_5Cl}$ = 23 was observed in excellent agrement with Streiwieser's average value of 30 in the condensed phase[35] and similar to certain values of $k_{CH_3X}/k_{C_2H_5X}$ found with $PhN^{-}\cdot$[36] in the gas phase. However, a component of E2 elimination cannot be ruled out in these reactions of the strongly basic $Ph_2C^{-}\cdot$ with C_2H_5Br and C_2H_5Cl.

D. Carbonyl Nucleophilic Addition/Radical β-Fragmentation Reactions with $Ph_2C^{-\bullet}$. The carbonyl group plays a central role in organic chemistry because it is involved in a wide variety of reactions and functional group conversions. There has been considerable activity in the mechanistic study of carbonyl group reactions in solution. A major reaction of the carbonyl group in organic molecules is that of nucleophilic addition.[37] The generally accepted mechanism for this reaction involves equilibrium formation of a tetrahedral intermediate.[38]

Prior to 1983, the gas-phase studies of nucleophilic carbonyl addition reactions were limited to only a few examples. Bowie and coworkers[39] reported the formation of minor amounts of adducts of acetic and trifluoroacetic anhydrides in an ICR spectrometer and suggested that these adducts were collisionally stabilized tetrahedral adducts. In 1983, McDonald and Chowdhury reported that F_3C^- reacted with a number of carbonyl containing molecules by carbonyl addition forming the adduct ions.[7] For one of these adducts, $(CF_3)_3CO^-$, which was exclusively and rapidly formed in the reaction of F_3C^- with $(CF_3)_2CO$, the PA was bracketed and shown to be the same as that of the authentic alkoxide, $(CF_3)_3CO^-$, produced by deprotonation of the alcohol. This result characterized the adduct as the tetrahedral alkoxide, and established the nucleophilic carbonyl addition mechanism as common to both the condensed and gas phases.

Prior to and since this important result, McDonald and coworkers have examined the reactions of several hypovalent anion radicals, e.g. $PhN^{-\bullet}$ and $S^{-\bullet}$[36], with carbonyl-containing molecules. The present results extent these studies with $Ph_2C^{-\bullet}$ as the hypovalent reactant. The idea behind the use of hypovalent anion radicals, e.g. $Ph_2C^{-\bullet}$, in the carbonyl addition reactions is to eliminate the reversal of the adduct forming step, by having a lower

threshold channel, β-fragmentation of the anion radical adduct.[36] These general steps are shown in eq. 18 with $Ph_2C^{-}\cdot$. The relative amounts of the

$$Ph_2C^{-}\cdot + \begin{matrix} R_1 \\ R_2 \end{matrix}CO \longrightarrow Ph_2\dot{C}\text{-}\overset{O^-}{\underset{R_2}{C}}\text{-}R_1 \longrightarrow \begin{cases} Ph_2C{=}C(O^-)R_1 + R_2\cdot \\ Ph_2C{=}C(O^-)R_2 + R_1 \end{cases} \qquad (18)$$

enolate anions observed are related to the $D°(C\text{-}R_1)$ and $D°(C\text{-}R_2)$ values in the adduct anion radical.

1. Reactions of $Ph_2C^{-}\cdot$ with Aldehydes. The reactions of $Ph_2C^{-}\cdot$ with three aldehydes, CH_3CHO, C_2H_5CHO, and $(CH_3)_3CCHO$, were examined. All three reactions were fast with rate constants close to their collision limits. Two types of products were observed. In the reactions with CH_3CHO and C_2H_5CHO, H^+-transfer was competitive with the carbonyl addition followed by radical β-fragmentation reaction channel because $Ph_2C^{-}\cdot$ is a strong base. Two ion products, m/z 195, and m/z 43 were observed in the reaction of $Ph_2C^{-}\cdot$ with CH_3CHO, and were assigned the structures of the enolate ions, $Ph_2C{=}C(O^-)H$ (eq 19a) and $CH_2{=}C(O^-)H$ (eq 19b), respectively.

$$Ph_2C^{-}\cdot + CH_3CHO \longrightarrow Ph_2C{=}C(O^-)H + CH_3\cdot \qquad (19a)$$
$$\Delta H° = -22.0 \text{ kcal mol}^{-1}$$
$$\longrightarrow CH_2{=}C(O^-)H + Ph_2CH\cdot \qquad (19b)$$
$$\Delta H° = -13.6 \text{ kcal mol}^{-1}$$
$$\not\longrightarrow Ph_2C{=}C(O^-)CH_3 + H\cdot \qquad (19c)$$
$$\Delta H° = -14.0 \text{ kcal mol}^{-1}$$

The related ion products m/z 195 and 57 were observed in the reaction of $Ph_2C^{-\cdot}$ with C_2H_5CHO and were assigned structures of the enolate anions $Ph_2C(O^-)H$ (eq 20a) and $CH_3CH{=}C(O^-)H$ (eq 20b), respectively. The reaction of

$$Ph_2C^{-\cdot} + CH_3CH_2CHO \longrightarrow Ph_2C{=}C(O^-)H + C_2H_5\cdot \qquad (20a)$$
$$\Delta H^\circ = -24.5 \text{ kcal mol}^{-1}$$
$$\longrightarrow CH_3CH{=}C(O^-)H + Ph_2CH\cdot \qquad (20b)$$
$$\Delta H^\circ = -14.1 \text{ kcal mol}^{-1}$$
$$\not\longrightarrow Ph_2C{=}C(O^-)C_2H_5 + H\cdot \qquad (20c)$$
$$\Delta H^\circ = -16.5 \text{ kcal mol}^{-1}$$

$Ph_2C^{-\cdot}$ with $(CH_3)_3CCHO$ occurred exclusively by the carbonyl addition/fragmentation mechanism with formation of m/z 195, $Ph_2C{=}C(O^-)H$, and loss of the tert-butyl radical (eq 21).

$$Ph_2C^{-\cdot} + (CH_3)_3CCHO \longrightarrow Ph_2C{=}C(O^-)H + (CH_3)_3C\cdot \qquad (21)$$

Two other reaction channels, which are thermochemically possible in these reactions were not observed: (i) H-atom abstraction by $Ph_2C^{-\cdot}$ from the carboxaldehyde function, and (ii) fragmentation of an H-atom from the tetrahedral adducts formed from the addition of $Ph_2C^{-\cdot}$ to the carbonyl groups of these aldehydes. The later fragmentation of an H-atom had been observed in the reaction of $PhN^{-\cdot}$ with all three aldehydes by McDonald[36] and with CH_3CH_2CHO by Brauman.[40] However, this reaction channel is not expected compared to that of loss of an alkyl radical from the tetrahedral intermediate in eq 18 where R_1 = H and R_2 = alkyl, if the intermediate

adduct is in its ground state since DH°(C-H) > DH° (C-alkyl) by 10 to 15 kcal mol^{-1} in organic molecules. H-atom abstraction by $Ph_2C^{-}\cdot$ from RCHO (i above) appears to be reasonably exothermic ($DH°(Ph_2C^{-}-H)$ = 96.4 ± 4 kcal mol^{-1} and DH°(RC(=O)H) = ~87 kcal mol^{-1}).[15,25] However, no H-atom abstraction was observed. Thus, $Ph_2C^{-}\cdot$ reacts as a strong nucleophile towards carbonyl center of aldehydes, but not as a radical.

2. Reactions of $Ph_2C^{-}\cdot$ with Ketones. CF_3COCH_3 reacts at unit efficiency with $Ph_2C^{-}\cdot$ exclusively by H^+-transfer giving the enolate anion $CF_3C(O^-)=CH_2$. This was expected since this ketone is quite acidic ($\Delta H°_{acid}$ = 350.3 kcal mol^{-1})[15a] and H^+-transfer to $Ph_2C^{-}\cdot$ is 30 kcal mol^{-1} exothermic.

The fast reaction of $Ph_2C^{-}\cdot$ with acetone proceeded by 90% H^+-transfer and 10% addition/fragmentation even though the protons of acetone are less acidic than that of those aldehydes. This result indicates that the carbonyl function of the acetone is not as reactive as that of the three aldehydes investigated. This has been well known in solution chemistry and was observed for some gas-phase reactions.[36] If we factor k_{total} for the component involving the addition/fragmentation channel of this reaction, $k^{C=O}_{Ph_2C^{-}\cdot}$ = 6.3 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Similar factoring of k_{total} for the reaction of $PhN^{-}\cdot$ with acetone gives $k^{C=O}_{PhN^{-}\cdot}$ = 5.7 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[36] Thus, $Ph_2C^{-}\cdot$ is kinetically a better (stronger) nucleophile in addition to the carbonyl group of acetone by a factor of 11 than is $PhN^{-}\cdot$. This increased nucleophilicity of $Ph_2C^{-}\cdot$ compared to $PhN^{-}\cdot$ is probably due mainly to a greater affinity of $Ph_2C^{-}\cdot$ for the carbonyl carbon of acetone than that of $PhN^{-}\cdot$ rather than a change in the intrinsic barrier heights in the two reactions. This is also seen in the larger methyl cation affinity

of $Ph_2C^{-\cdot}$ (MCA = 284 kcal mol^{-1}) compared to that of $PhN^{-\cdot}$ (MCA = 268.5 kcal mol^{-1}).

The third ketone examined was the α-diketone, biacetyl ($CH_3C(=O)C(=O)CH_3$). The fast reaction of $Ph_2C^{-\cdot}$ with biacetyl occurred by two channels, H^+-transfer giving the conjugate base of biacetyl (major; eq 22a) and carbonyl addition followed by radical β-fragmentation yielding the enolate anion $Ph_2C{=}C(O^-)CH_3$ and assumed loss of acetyl radical (minor; eq 22b). Biacetyl has previously been shown to react rapidly with $PhN^{-\cdot}$ (k_{total} = 6.4 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}) with 98% of the reaction occurring by the addition/fragmentation mechanism and 2% by H^+-transfer.[36] The additional

$$Ph_2C^{-\cdot} + CH_3COCOCH_3 \xrightarrow{0.77} \underset{(\underline{m/z}\ 85)}{CH_3COC(O^-){=}CH_2} + Ph_2CH\cdot \qquad (22a)$$

$$\xrightarrow{0.23} \underset{(\underline{m/z}\ 209)}{Ph_2C{=}C(O^-)CH_3} + CH_3CO\cdot \qquad (22b)$$

amount of H^+-transfer in the reaction of $Ph_2C^{-\cdot}$ with biacetyl compared to that of $PhN^{-\cdot}$ is reasonable since $Ph_2C^{-\cdot}$ is a stronger base (δPA = 8 kcal mol^{-1}). It is interesting, however, that nucleophilic carbonyl addition remains competitive with H^+-transfer.

3. Reactions of $Ph_2C^{-\cdot}$ with Esters. The reactions of $Ph_2C^{-\cdot}$ with esters are interesting because the stage is set for a direct comparison of two different nucleophilic processes, (a) S_N2 displacement at Cα of the alkyl group (and/or E2 elimination with alkyl groups larger than CH_3) and (b) addition/fragmentation at the carbonyl center. Since the kinetic

nucleophilicity of $Ph_2C^{-}\cdot$ in S_N2 reactions with CH_3Br and CH_3Cl was judged to be medium, process (b) might become dominant in these studies.

The reaction of $Ph_2C^{-}\cdot$ with $CH_3CO_2CH_3$ was fast, $k_{total} = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (reaction 17, Table I). The major product channel was exothermic H^+-transfer producing the conjugate base of methyl acetate (eq 23a) while the minor channel involved less exothermic addition/fragmentation (eq 23b). In most respects, it is remarkable that the product of carbonyl

$$Ph_2C^{-}\cdot + CH_3CO_2CH_3 \xrightarrow{0.97} CH_2{=}C(O^-)OCH_3 + Ph_2CH\cdot \qquad (23a)$$

$$\xrightarrow{0.03} Ph_2C{=}C(O^-)CH_3 + CH_3O\cdot \qquad (23b)$$

addition/fragmentation was observed at all. The related reaction of $PhN^{-}\cdot$ with $CH_3CO_2CH_3$ occurred largely (88%) by the addition/fragmentation pathway with only 12% by the H^+-transfer channel.[36] However, the rate constant for this latter reaction was just measurable in the FA ($k_{total} = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}). Factoring the k_{total}'s for these two reactions with $CH_3CO_2CH_3$ into their $k^{C=O}$ components ($Ph_2C^{-}\cdot$, $k^{C=O} = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $PhN^{-}\cdot$, $k^{C=O} = 1.3 \times 10^{-13}$ cm^{-3} molecule^{-1} s^{-1}), $Ph_2C^{-}\cdot$ is found to be kinetically a better nucleophile than in carbonyl addition/fragmentation with $CH_3CO_2CH_3$ by a factor of 30.

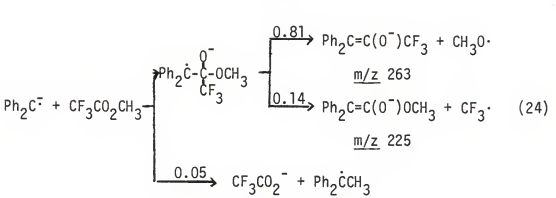
The reaction of $Ph_2C^{-}\cdot$ with HCO_2CH_3 was of interest since three separate reaction channels are possible, (a) carbonyl addition/fragmentation yielding $Ph_2C{=}C(O^-)H$ (m/z 195) and/or $Ph_2C(O^-)OCH_3$ (m/z 225), (b) S_N2 displacement at CH_3 producing HCO_2^- (m/z 45)[42], and (c) products of Riveros reaction[45] since $Ph_2C^{-}\cdot$ is a strong base. Channel (b) is least likely since $Ph_2C^{-}\cdot$ was previously shown to be a relatively poor S_N2 nucleophile methyl halides.

The Riveros reaction of $Ph_2C^{-\bullet}$ with HCO_2CH_3 would involve H^+-transfer/decarbonylation yielding CO and the complex $Ph_2CH\bullet/^-OCH_3$, the same comples suggested formed in proton transfer between $Ph_2C^{-\bullet}$ and CH_3OH. Since this complex was believed to produce Ph_2CH_2, H_2CO, plus an electron, the presence of this channel would be evidenced by a loew percent product ion recovery from channel (a), and/or attachment of the ejected electron with a neutral molecule (e.g. SF_6) and observation of that anion product.

The result of the fast reaction of $Ph_2C^{-\bullet}$ with HCO_2CH_3 ($k = 1.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) was exclusive formation of m/z 195, $Ph_2C{=}C(O^-)H$, produced by the carbonyl addition/fragmentation mechanism. The product percent recovery was excellent (~95%). Addition of SF_6 through a port down stream from the ion-molecule reaction region did not yield SF_6^-. Therefore, it is concluded that the Riveros reaction and S_N2 displacement do not compete with the nucleophilic carbonyl addition in this reaction. Comparison of the results of the reactions of $Ph_2C^{-\bullet}$ and $PhN^{-\bullet}$ with HCO_2CH_3 (for $PhN^{-\bullet}$), $k^{C=O} = 1.3 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}),[36] $Ph_2C^{-\bullet}$ is again shown to be kinetically a stronger nucleophile by a factor of 119. This rate ratio is probably more correct than that given above for the related reactions with $CH_3CO_2CH_3$ since the major or exclusive channels in the reactions of HCO_2CH_3 involve addition/fragmentation, and the reaction of $PhN^{-\bullet}$ with $CH_3CO_2CH_3$ occurred at the lower limit of the rate constant measurements in the FA and the product distribution could have a sizeable error.

As expected, the reaction of $Ph_2C^{-\bullet}$ with $CF_3CO_2CH_3$ occurred at nearly the collision limit (reaction 19, Table I). Since $CF_3CO_2^-$ is an excellent leaving group in S_N2 displacement reactions,[11] this reaction should test the nucleophilicity of $Ph_2C^{-\bullet}$ toward the S_N2 displacement at CH_3 vs. that of

carbonyl addition/fragmentatoin. The results are shown in eq 24. Only 5% of this reaction occurred by the S_N2 displacement channel. Ninety-five



(24)

percent of the reaction occurred by nucleophilic addition of $Ph_2C^{-\cdot}$ at the carbonyl center of this ester followed by radical β-fragmentation and loss of the CH_3O and CF_3. Note that this reactionn occurred on essentially every collision. We are not able to compare the $k^{C=O}$'s here between $Ph_2C^{-\cdot}$ and $PhN^{-\cdot}$ since both occurred at or near the collision limit. However, the ratio of the fragmentation channels was 99/1 (of $CH_3O\cdot$ vs. that of $CF_3\cdot$) with $PhN^{-\cdot}$[36] compared to 6/1 in eq 24.

The fast reaction of $Ph_2C^{-\cdot}$ with the ethyl ester $CF_3CO_2C_2H_5$ proceeded exclusively by the carbonyl addition/fragmentation mechanism (reaction 20, Table I) with the ratio of fragmentation channesl (25a/25b) as 9/1. It was not surprising to find the absence of an S_N2 displacement reaction channel here since ethyl derivatives react slower than methyl derivatives in S_N2 processes.[35] A large reaction barrier can also be expected for an E2 elimination process since E2 eliminations are ~20 kcal mol^{-1} less exothermic than the corresponding S_N2 displacement channels. This was similar to the results obtained in the reaction of $PhN^{-\cdot}$ with $CF_3CO_2C_2H_5$.[36]

The fast reaction of $Ph_2C^{-\cdot}$ with the thio-ester $CF_3C(=O)SC_2H_5$ is, in part, expected, and, in part, strange (eq 26). The two major product

$$Ph_2C^{-\cdot} + CF_3CO_2C_2H_5 \xrightarrow{0.9} Ph_2C=C(O^-)CF_3 + C_2H_5O\cdot \qquad (25a)$$

$$\xrightarrow{0.1} Ph_2C=C(O^-)OC_2H_5 + CF_3\cdot \qquad (25b)$$

$$Ph_2C^{-\cdot} + CF_3COSC_2H_5 \xrightarrow{0.45} Ph_2C=C(O^-)CF_3 + C_2H_5S\cdot \qquad (26a)$$

$$\xrightarrow{0.45} CF_3COS^- + Ph_2\dot{C}C_2H_5 \qquad (26_b)$$

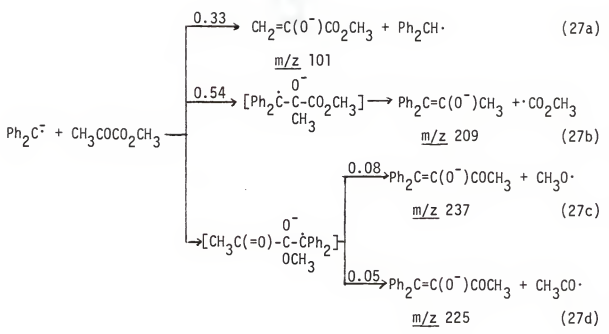
$$\xrightarrow{0.10} CF_3COS\bar{C}HCH_3 + Ph_2CH\cdot \qquad (26c)$$

$$(\underline{m/z}\ 157)$$

forming channels are easily explained. Channel 26a is the result of addition/fragmentation with specific loss of $C_2H_5S\cdot$ from the tetrahedral adduct, and eq 26b is the result of either S_N2 displacement or E2 elimination since CF_3COS^- should be a much better anionic leaving group than was $CF_3CO_2^-$ from the reaction of $CF_3CO_2C_2H_5$; $\Delta H^\circ_{acid}(CF_3COSH)$ is unknown.

Channel 26c is the unexpected one. All that can be presently said is that the conjugate base of the ester is formed. It is assumed that the anion is on Cα since the C_β anion would be expected to complete the E2 elimination (Elcb) process yielding CF_3COS^- plus ethylene. Formation of this product ion is not understood.

The fast reaction of $Ph_2C^{-\cdot}$ with methyl pyruvate ($CH_3C(=O)CO_2CH_3$) proceeded by pathways quite analogous to the results obtained in the related reaction of $PhN^{-\cdot}$ with this α-keto ester.[36] The present results (reaction 22, Table I) are summarized in eq 27. Four product ions were observed and



their structures were assigned as m/z 101 ($H_2C{=}C(O^-)CO_2CH_3$), 209 ($Ph_2C{=}C(O^-)CH_3$), 225 ($Ph_2C{=}C(O^-)OCH_3$), and 237 ($Ph_2C{=}C(O^-)C(=O)CH_3$). Formation of m/z 101, the conjugate base of the ester, appears to involve simple H^+-transfer reaction (eq 27a). The remaining three product ions are considered to arise by the scheme given in eqs 27b-27d. The predominant addition/fragmentation at the keto-carbonyl over that of the ester-carbonyl is that expected from the relative reactivities of $PhN\dot{\cdot}^-$ [4] and $Ph_2C^{-}\cdot$ with the individual carbonyl functional groups.

E. Reactions of $Ph_2C^{-}\cdot$ with CO_2, COS, CS_2, and O_2. $Ph_2C^{-}\cdot$ rapidly reacts with CO_2 to form 99% adduct $Ph_2CCO_2^{-}\cdot$ (eq 28a) and 1% Ph_2CO^{-} (eq. 28b), the latter being the oxygen-atom abstraction product. The formation

$$Ph_2C^{-}\cdot + CO_2 \xrightarrow[He]{0.99} Ph_2CCO_2^{-}\cdot \quad \underline{m/z}\ 210 \qquad (28a)$$

$$\xrightarrow{0.01} Ph_2C{=}O^{-}\cdot + CO \quad \underline{m/z}\ 182 \qquad (28b)$$

of the adduct $Ph_2CCO_2^{-\cdot}$ involves nucleophilic addition on the carbon of CO_2. Since radical fragmentation of this adduct does not occur, the excess energy in the adduct acquired through formation of the carbon-carbon bond must be removed by collisions with the buffer gas or dissociation to the reactants will occur. A P_{He} effect was not observed; the rate constant changed from 3.9×10^{-10} cm^3 molecule^{-1} s^{-1} at P_{He} = 0.5 torr to 4.7×10^{-10} cm^3 molecule^{-1} s^{-1} at P_{He} = 1.0 torr, and these values are within the experimental error limits of ± 30%. This means that the termolecular addition may be saturated at the lowest pressure, P_{He} = 0.5 torr. The detection of $Ph_2CO^{-\cdot}$ seems surprising since the $Ph_2C^{-\cdot}$ apparently abstracted an oxygen atom from the extremely stable molecule CO_2. The reaction in eq 28b is possible energetically if Ph_2CO has an EA > 0.45 eV[41]; EA(Ph_2CO) is unknown.

The reaction of $Ph_2C^{-\cdot}$ with COS followed the same pattern as that observed with CO_2. Attracted by ion-dipole and ion-induced dipole forces, $Ph_2C^{-\cdot}$ attacks the carbonyl carbon of COS forming the adduct (eq 29a) or at the sulfur atom forming $Ph_2CS^{-\cdot}$ with expulsion of CO (eq 29b). The observa-

$$Ph_2C^{-\cdot} + COS \xrightarrow[He]{0.85} \underset{\underline{m/z}\ 226}{Ph_2CCOS^{-\cdot}} \qquad (29a)$$

$$\xrightarrow{0.15} \underset{\underline{m/z}\ 198}{Ph_2CS^{-\cdot}} + CO \qquad (29b)$$

tion of 15% sulfur atom abstraction is not surprising since D° (S=CO) < D°(O=CO) by 53 ± 1 kcal mol^{-1}.

There was a great change in the product branching ratio when the neutral was CS_2 (eq 30), although a similar course was followed as described

$$Ph_2C^{-\cdot} + CS_2 \xrightarrow[He]{0.04} Ph_2CCS_2^{-\cdot} \quad \underline{m/z}\ 242 \qquad (30a)$$

$$\xrightarrow{0.96} Ph_2CS^{-\cdot} + CS \quad \underline{m/z}\ 198 \qquad (30b)$$

above for CO_2 and COS. Only 4% of the adduct ion, m/z 242, was observed while 96% was $Ph_2CS^{-\cdot}$ formed by sulfur-atom abstraction. This is probably due to the fact that the carbon atom in CS_2 bears less positive charge than that in COS or CO_2, and $Ph_2C^{-\cdot}$ attacks sulfur atom preferably. In fact, the C=S bond in CS_2 is stronger than that in COS by 20 kcal mol^{-1}.

The reaction of $Ph_2C^{-\cdot}$ with O_2 formed five product ions, m/z 198 ($Ph_2CO_2^{-\cdot}$) 121 ($PhCO_2^{-\cdot}$), 93 (PhO^-), 77 (Ph^-), and 16 (O^-)(Figure 5 and 6). The reaction was slow despite the fact that all reaction channels appear to be significantly exothermic(Table I). This seems in agreement with the observation that $Ph_2C^{-\cdot}$ is a strong base and nucleophile but a unreactive radical since the adduct ($Ph_2CO_2^{-\cdot}$) formation is a radical combination of the triplet O_2 and doublet $Ph_2C^{-\cdot}$. The excess energy of the adduct acquired through C-O bond formation could be disposed in three ways, (i) removed by collisions with the buffer gas, (ii) dissociation to the reactants, and (iii) used in overcoming the barriers to form products.

$$Ph_2C^{-\cdot} + O_2 \quad Ph_2CO_2^{-\cdot} + PhCO_2^- + PhO^- + Ph^- + O^- + Ph\cdot + Ph\dot{C}O + CO_2 \qquad (31)$$

(at 0.5 torr 29% 36% 21% 10% 4%)

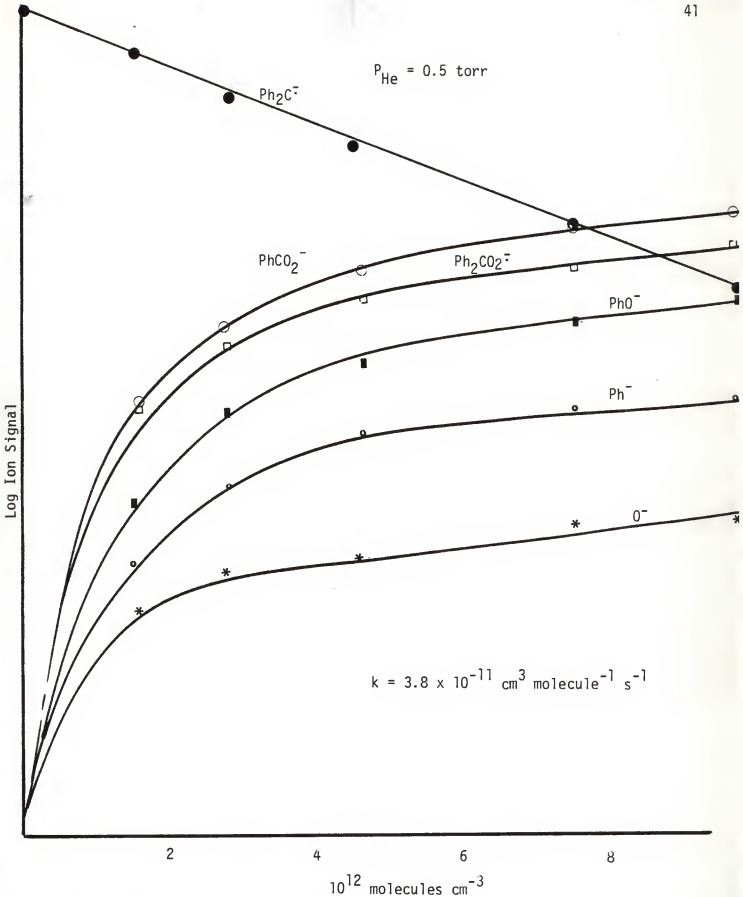


Figure 5. Semilog plot of decay of Ph_2C^- and formation of product ions for the reaction of Ph_2C^- with O_2.

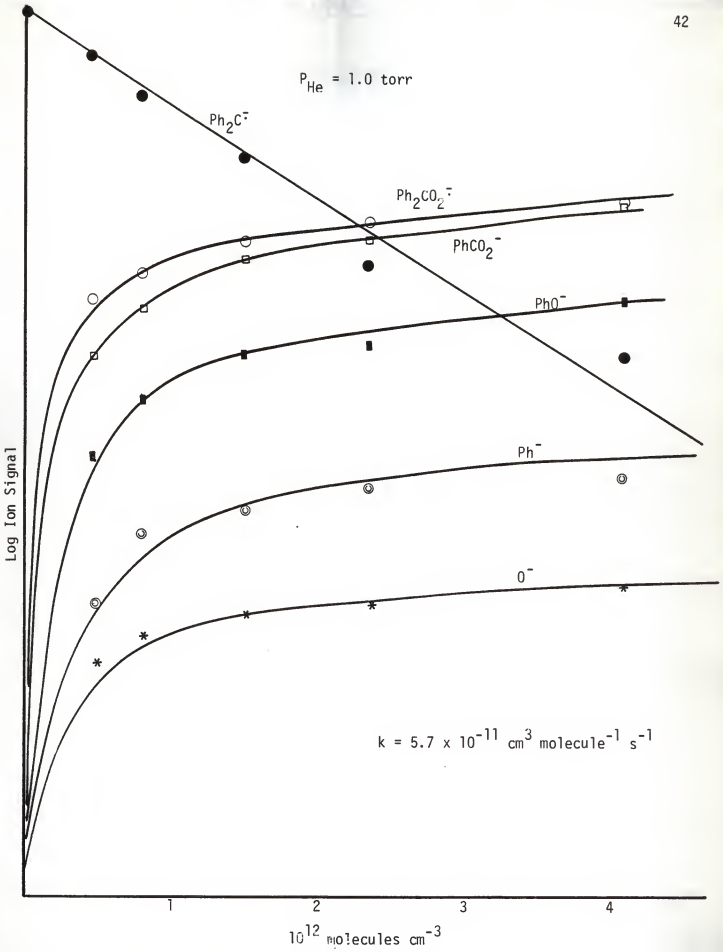


Figure 5. Semilog plot of decay of Ph_2C^- and formation of product ions for the reaction of Ph_2C^- with O_2.

A P_{He} dependence was observed in the product branching ratio and possible in the change of rate constants. The observed fractions of the total product forming channels at P_{He} = 1.0 torr were 39% channel 31a, 34% channel 31b, 18% channel 31c, 6% channel 31d, and 3% channel 31e (Figure 6). The observed rate constants were 3.8×10^{-11} cm^3 molecule^{-1} s^{-1} at P_{He} = 0.5 torr and 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} at P_{He} = 1.0 torr. However, the variation is within the error limit of ± 30%. We were not able to carry out the experiment at lower than 0.5 torr of higher than 1.0 torr pressures. The average rate constant is reported in Table I. The mechanisms involved in producing the various fragmentation product ions are not understood.

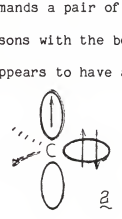
F. Summary. Diphenylcarbene anion radical ($Ph_2C^{-\cdot}$) was generated in the gas phase by DEA using a flowing afterglow apparatus, and its PA was determined from bracketing studies of ion-molecule reactions with potential H^+-donor molecules of know acidity. From PA($Ph_2C^{-\cdot}$) = 382 ± 2 kcal mol^{-1}, $\Delta H_f^\circ(Ph_2C^{-\cdot})$ = 84 ± 2 kcal mol^{-1} was calculated. The thermochemical data of $Ph_2C^{-\cdot}$ are summarized in Table III.

Table III Thermochemical Data of Diphenylcarbene Anion Radical

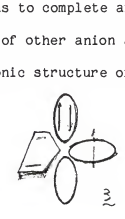
PA($Ph_2C^{-\cdot}$) = 382 ± 2 kcal mol^{-1} [a]
$\Delta H_f^\circ(Ph_2C^{-\cdot})$ = 84 ± 2 kcal mol^{-1} [a]
PA(Ph_2CH^-) = 366.5 ± 4 kcal mol^{-1} = $\Delta H^\circ_{acid}(Ph_2CH_2)$ [b]
$DH^\circ(Ph_2C^{-}\text{-}H)$ = 96.4 ± 4 kcal mol^{-1} [c]
$\Delta H_f^\circ(Ph_2CH^-)$ = 39 ± 4 kcal mol^{-1}
$DH^\circ(Ph_2CH\text{-}H)$ = 81.4 kcal mol^{-1}

[a] Table II of this work. [b] Reference 15. [c] Reference 15, 25. [d] References 15, 25, and 26b.

The reactions of $Ph_2C^{-\cdot}$ with $(CH_3)_2CHOH$ and C_2H_5OH proceed by mainly proton transfer channel and the result of the reaction with CH_3OH provided further evidence for the gas-phase reductive β-dehydrogenation process. No H-atom transfer between alcohols and $Ph_2C^{-\cdot}$ was observed. The reactions of $Ph_2C^{-\cdot}$ with CH_3X molecules established $Ph_2C^{-\cdot}$ as having medium nucleophilicity towards sp^3-carbon in CH_3X according to Bohme's scale.[32] This means that the S_N2 reactions of $Ph_2C^{-\cdot}$ with CH_3X molecules have relatively large intrinsic barriers,[33] which are partially compensated for by the significant exothermicities of these reactions. Modest kinetic nucleophilicity of $Ph_2C^{-\cdot}$ in S_N2 reactions, in fact, was observed from rate constants measurements. The reactions of $Ph_2C^{-\cdot}$ with aldehydes, ketones, and esters proceed rapidly by both H^+-transfer and nucleophilic addition to the carbonyl center followed by β-radical fragmentation channels. The nucleophilicity of $Ph_2C^{-\cdot}$ towards sp^2-carbon of carbonyl function is shown to be much stronger (~100 times) than that of $PhN^{-\cdot}$ in the gas-phase ion-molecule reactions. The fact that $Ph_2C^{-\cdot}$ behaves as a base, but not as a radical, can be attributed to the electron structure feature of $Ph_2C^{-\cdot}$. The structure of $H_2C^{-\cdot}$ ($^2B_1$) (2) was calculated to have the H-C-H angle of about 100°, very similar to that in H_2C ($^1A_1$) of 102°, with a σ^2p^1 electronic configuration.[46] Cyclopentadienylidene anion radical (c-$C_5H_4^{-\cdot}$, 3) has a σ radical ρ anion (σ^1p^2) ground-state structure since the p-orbital is a part of a π-system that demands a pair of electrons to complete an aromatic structure.[5] By comparisons with the behaviors of other anion and anion radicals (Table IV), $Ph_2C^{-\cdot}$ appears to have a electronic structure of σ anion p radical (σ^2p^1, 4)



2



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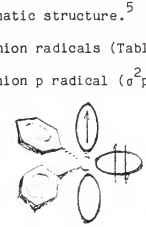

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Table IV. Rate Constants Data for S_N2 Displacement and H-atom Abstraction Reactions of CH_3X Molecules with Some Anion and Carbene Anion Radicals.

Anion or Carbene Anion Radical	CH_3X	$k_{substitution}$ (cm^3 $molecule^{-1}$ s^{-1})	$k_{abstraction}$ (cm^3 $molecule^{-1}$ s^{-1})
S^- [a]	CH_3Br	4.2×10^{-10}	$< 10^{-13}$
Ph_2C^- [b]	"	3.9×10^{-10}	$< 10^{-13}$
PhN^- [a]	"	1.8×10^{-11}	$< 10^{-13}$
$(CF_3)_2C^-$ [e]	"	9×10^{-12}	$< 10^{-13}$
$c\text{-}C_5H_5^-$ [c]	"	2.5×10^{-12}	$< 10^{-13}$
$c\text{-}C_5H_4^-$ [d]	"	$- 1 \times 10^{-10}$	2×10^{-11}
Ph_2C^- [b]	CH_3Cl	3.2×10^{-11}	
S^- [a]	"	3.0×10^{-11}	$< 10^{-13}$
PhN^- [a]	"	$< 10^{-13}$	$< 10^{-13}$
$c\text{-}C_5H_5^-$ [e]	"	$<10^{-13}$	
$(CF_3)_2C^-$ [e]	"	$<10^{-13}$	$< 10^{-13}$
$c\text{-}C_5H_4^-$ [e]	"	$\sim 10^{-13}$	9×10^{-12}

[a] Reference 36. [b] Table I of this work. [c] Reference 47. [d] Reference 5. [e] Reference 8.

and the unpaired electron in the p-orbital is delocalized with the benzene π-system. However, the electron pair in the hybrid (approximately sp^2) orbital appears to be delocalized only to a lesser extent as the data shown in Table IV indicating that the nucleophilicity of $Ph_2C^{-}\cdot$ is as strong as those of electron-localized anions, e.g., $S^{-}\cdot$, and F_3C^{-}, and much stronger than those of electron-delocalized anions, e.g., $c\text{-}C_5H_5^{-}$, and $PhN^{-}\cdot$. Inspection of the molecular model of $Ph_2C^{-}\cdot$ shows that the p-orbital of the central carbon can be situated at the same plane with one phenyl group, while the sp^2-like orbital overlaps the second phenyl group (orthogonal to the first) only to a lesser extent. Therefore, it is reasonable to assume that $Ph_2C^{-}\cdot$ has a ground-state electronic structure of σ anion p radical (σ^2p^1) with the unpaired electron in the p-orbital delocalized to the phenyl group and the pair of electorns in the sp^2-like orbital localized. This structure agrees with the fact that $Ph_2C^{-}\cdot$ reacts as a strong nucleophile towards sp^2-carbon in carbonyl function, a strong base towards potential H^+-donors, but not as a radical towards potential H-atom donors. The relative large intrinsic barriers in S_N2 reactions compared to that in carbonyl additions/fragmentation reactions can be attributed to the steric effect arising from the two bulky phenyl groups of $Ph_2C^{-}\cdot$ which cause crowding of the five-ligand coordinated transition state in S_N2 displacement reactions.

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GENERATION AND REACTIONS OF DIPHENYLCARBENE ANION RADICAL ($Ph_2C^{\cdot -}$) IN THE GAS PHASE USING A FLOWING AFTERGLOW APPARATUS

by

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B. S., Nanking University, China, 1981

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

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Manhattan, Kansas

1984

ABSTRACT

Diphenylcarbene anion radical ($Ph_2C^{\cdot-}$) was generated in the gas phase by dissociative electron attachment with diphenyldiazomethane (Ph_2CN_2) in a flowing afterglow apparatus. From bracketing studies of ion-molecule reactions of $Ph_2C^{\cdot-}$ with potential proton-donor molecules of known acidity, $PA(Ph_2C^{\cdot-}) = 382 \pm 2$ kcal mol^{-1} was determined from which $\Delta H_f^\circ(Ph_2C^{\cdot-}) = 84 \pm 2$ kcal mol^{-1} was calculated. Although the reaction of $Ph_2C^{\cdot-}$ with $(CH_3)_2CHOH$ ($\Delta H^\circ_{acid} = 376.3 \pm 0.6$ kcal mol^{-1}) occurred exclusively by H^+-transfer, the reaction with CH_3OH ($\Delta H^\circ_{acid} = 381.4 \pm 0.6$ kcal mol^{-1}), (and to a lesser extent with C_2H_5OH ($\Delta H^\circ_{acid} = 378.3 \pm 0.6$ kcal mol^{-1})), proceeded rapidly by what is considered to be a reductive β-dehydrogenation process yielding Ph_2CH_2, H_2CO, and a detached electron. The presence of the detached electron was established by addition of SF_6, which attach electrons forming $SF_6^{\cdot-}$. Generation of $H_2CO^{\cdot-}$ as a metastable intermediate which ejects an electron is proposed.

The reactions of $Ph_2C^{\cdot-}$ with CH_3Br and CH_3Cl produced only the corresponding halide ions via S_N2 displacement reaction mechanism. Comparison of the rate constants for these reactions with those of other anionic nucleophiles with these methyl halides showed $Ph_2C^{\cdot-}$ to have medium S_N2 nucleophilicity. $Ph_2C^{\cdot-}$ was shown to be a strong nucleophile with carbonyl centers of various organic molecules. For similar R groups, the order of carbonyl reactivity was RCHO > RC(=O)R > RCO_2R. In contrast to other anion radicals studied in the gas phase, no H-atom transfer reactions were observed between $Ph_2C^{\cdot-}$ with alcohols, carbonyl compounds, and CH_3X molecules. This behavior of $Ph_2C^{\cdot-}$ as a nucleophile, but not as a radical, was considered to be the evidence suggesting that the $Ph_2C^{\cdot-}$ has a ground-state electron structure of σ anion p radical (σ^2p^1).